PROBLEMS WITH THE SCALE-UP IN THE PRODUCTION OF MULTI-WALLED CARBON NANOTUBES

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ABSTRACT. Catalytic chemical vapour deposition (CCVD) is the most important method to produce multi-walled carbon nanotubes (MWCNT) because this method works at lower temperature and can produce MWCNT in large scale. The large scale production of MWCNT goes hand in hand with a lot of technological problem. A large-scale laboratory device was planned and implemented on the basis of a smaller laboratory device; after which pilot device was planned based on the observations and the experiments conducted with the large-scale laboratory device.

Keywords: *multi-walled carbon nanotubes, CCVD synthesis, scale-up, CFD, k-ε turbulence model*

INTRODUCTION

Carbon nanotubes (CNT) were discovered in the soot of arch discharge by Sumio Iijima in 1991 [1]. Carbon nanotubes are allotropes of carbon and members of the fullerene structural family. Carbon nanotubes are categorized as single-walled nanotubes (SWCNT) and multi-walled nanotubes (MWCNT) [2]. MWCNTs consist variable number of graphene sheets rolled coaxially into a cylinder of nanometric diameter [3].

Several production methods have been developed aiming at the production of carbon nanotubes in large scale, such as laser vaporization [4], electric arc discharge [5] and catalytic chemical vapour deposition of hydrocarbons over metal catalysts (CCVD technique) [6]. The first two methods are high temperature processes and can produce high quality nanotubes. However, the yields are poor and hence they are not adaptable for large-scale production. In contrast the CCVD technique is an efficient method to produce multi-walled carbon nanotubes (MWCNTs) because this

method ensures a possibility to produce nanotubes at relatively low temperature in a large scale at relatively low cost. It is the most promising method to commercialize the carbon nanotubes. The CCVD method uses transition metal (Fe, Co or Ni) oxides supported on zeolite or silica [7].

The aim of all production technologies is formation of a more valuable material through some chemical reactions. The reactor is a place where reactions generally take place. Hence, a reactor must be able to convert the necessary amount of raw materials into products with desired quality in given amount of time. A chemical technology cannot be imagined without a reactor consequently the design process of a reactor has a really important role in generating a well profitable technology. Furthermore the planing of instrumentation and optimization of operating variables is also crucial. Main steps in development of a well functioning reactor are the following:

- defining desired performance of reactor operation;
- collecting all a prior information and physical constraints;
- determining and/or investigating flow field in the reactor;
- assigning all operating variables.

The scale-up of a reactor can be based on different considerations. Two systems are similar if a given parameter of the prototype is bigger by a proportionality factor than that of the model, and there are as many relationships of this kind as many degrees of freedom the system has. There is geometric, mechanical, thermal and chemical similarity, so the conditions for the reactor total similarity of the two reactors are:

- the condition for geometric similarity is that the representative sizes in the two system be proportional;
- the condition for mechanical similarity is that the Re numbers be identical in the two systems;
- the condition for thermal similarity is that the Da_{III} numbers be identical in the two systems;
- the condition for chemical similarity is that the Da_{I} numbers be identical in the two systems.

It has been proven that the four similarities cannot exist at the same time, thus making the total similarity impossible. When upscaling, we have to put up with partial similarity, the most important task being the determination of the key parameters.

If we want to reach chemical similarity, the product of the average residence time and the reaction rate has to be constant in the two systems. The average residence time is determined by the flow circumstances. The reaction rate is affected by the temperature and the initial concentrations. The two systems are chemically similar if they have identical average residence time, temperature and initial concentrations [8].

Nowadays development of flow field in process equipments is a key issue in planning of process unit. With a well designed flow field the overall

process performance and safety of operation can be increased at the same time. To support this step, different modeling softwares and flow sheet simulators have been developed in last decades. As computational capacity of computers has being increased the role of computational fluid dynamics (CFD) in applied modeling technics and methods has significantly grown since the first computer was switched on [9].

CFD is a collection of numerical solvers for partial differential equations. With applying CFD codes more complicated problems in more complex structures can be investigated in details than with other modeling technics. Coupling of mathematical models of different physical and chemical processes with efficient numerical solvers makes possible to analyze chemical engineering and other kind of engineering problems in much more details. Of course, as in other modeling technics, CFD models must be validated before it can be used to predict the behavior of invesigated system. Validation of models is based on comparing simulation results with measured variables, i.e. developing an adequate CFD model, because of the complexity of model, needs well-designed and precisely carried out experiments.

RESULTS AND DISCUSSION

A large-scale laboratory device was planned on the basis of the a smaller laboratory device; after which pilot device was planned based on the observations and the experiments conducted with the large-scale laboratory device. The laboratory-scale experiments were conducted at the Department of Applied and Environmental Chemistry of the University of Szeged. Nanotubes were synthesized in a fixed bed horizontal quartz tube reactor with a diameter of 60 mm and a length of 1100 mm. The catalyst was placed in a quartz boat and shoved into the middle of the reactor [10]. The scheme of the laboratory-scale device is shown in Fig. 1.

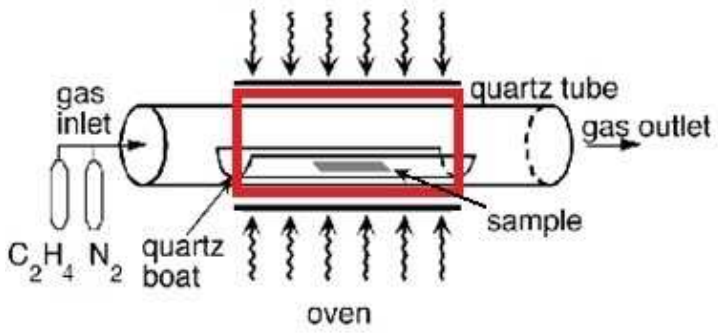

Figure 1. The scheme of the laboratory-scale device

The first step of upscaling was the planning of a large-scale laboratory device the volume of which is fifty times bigger. The followings were concluded about the already existing laboratory device:

- The length of 1100 mm is unnecessary because the reaction takes place in the middle of the pipe reactor (on the surface of the catalyst in the quartz boat).
- The carbon nanotube as a solid powder-like substance is formed in the reaction. The horizontal upscaling is not practical since the flowing gases might sweep off the product.
- The catalyst granules are lying on one another. If the amount of the catalyst is higher, the granules in the lower layers make almost no contact with the incoming gas. By moving the granule set, more intensive contact can be achieved. This can be done by rotating the reactor.
- The reactor is a semi-continuous reactor. The catalyst is in the reactor, the product is formed on its surface. The gas is supplied in a steady volume flow into the reactor, and the gas leaves the reactor in a steady volume flow. Because of this, the large-scale laboratory device was designed in a different construction.
- Quartz, as a structural material is expensive and difficult to shape. Since the reaction also takes place in metal reactors, refractory steel was chosen as the structural material of the reactor.

The design was carried out on the basis of geometrical similarity. The diameter of the quartz tube of the laboratory device (abbreviated as ld.) is d_{ld}=60 mm, the effective tube length is l_{ld}=60 mm, thus l_{ld}/d_{ld}=1. The volume of the laboratory device is V_{ld}=0.17 dm^3. The product however might only take up to the volume of the quartz tube, thus the maximal effective volume can be at most 50 % of the total volume. In reality, the volume of the product was only a fraction of this. When designing the large-scale reactor (abbreviated as lsr.), we used l_{lsr}/d_{lsr}=1 according to the geometrical similarity. Our aim was to design a device of fifty times the volume (V_{lsr}=8.5 dm^3) of the original. Supposing that the efficiency is also 50 % in the large-scale laboratory device, the volume of the device is V_{lsr}=8.5 dm^3 in a horizontal layout. Since $V_{lsr}=50V_{ld}$ and l_{lsr}/d_{lsr} =1, then it follows that $50d_{ld}^3=d_{lsr}^3$. The diameter of the large-scale reactor is d_{lsr}=220 mm, its length is also l_{lsr}=220 mm. These sizes are given for the large-scale reactor with horizontal layout (Fig. 2a).

The reactor is a semi-continuous reactor. The catalyst is in the reactor, the product is formed on its surface. The gas is fed into the reactor in a steady volume flow; and the gas also leaves the reactor in a steady volume flow. Because of this, the large-scale laboratory device was designed in the different construction that is given in Fig. 2b. The incoming gas enters and leaves on the same side of the reactor. The end of the reactor is closed. The incoming gases enter through the feed tube, which is

close to the closed end of the reactor. The outgoing gases leave by the curved surface of the feed tube, which is bordered by another tube (“reactor neck”) from the outside.

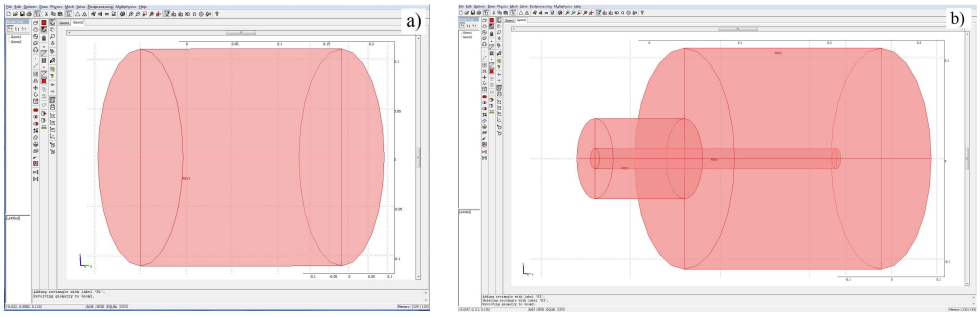

Figure 2. a) Scheme of the horizontal layout large-scale reactor b) Scheme of the horizontal layout large-scale reactor with feed tube and “reactor neck”

The reactor is supported at the reactor neck; there is no support from the closed side. The diameter of the reactor neck should be at least that big, that even if the reactor is supported 2000 mm away from its closed side, it should hold the whole reactor safely and stably. According to mechanical consideration, the diameter of the reactor neck is d_{neck}=80 mm. In the horizontal layout, the effective volume of the reactor with the reactor neck ($V_{lsr+neck,eff}$) is the volume of the 70 mm high, circular segment-based prism, which reaches the reactor neck $V_{lsr+neck,eff}$=2.3 dm^3 (Fig. 3a). Because of this, the effective volume decreased from the planned 50 % to 27 %. The effective volume can be increased by tilting the reactor. The effective volume of the reactor was examined at different inclination angles with the help of the Pro Engineer design software. The effective volume must be at least 50 % of the total volume. Our aim was to determine the necessary inclination angle. The effective volume increases to 60 % after tilting at a 30° angle (Fig. 3b). Considering the already availa ble furnace, the sizes had to be adjusted. The diameter of the tilted large-scale reactor was chosen to be $d_{lsr,tilted}$=200 mm, its length $l_{lsr,tilted}$=180 mm. The thickness of the wall of the reactor was 3 mm throughout the implementation; this makes the total volume $V_{lsr,titled}$=5.1 dm^3 and the effective volume $V_{lsr,titled,eff}$=2.9 dm^3. The implemented large-scale laboratory device is presented in Fig. 4.

Theoretically, the effective volume of 2.9 dm^3 means only 34-fold increase of volume instead of fifty. In practice however, the product never reached the 50 % of the total volume, only a fraction of it. Nevertheless, in the large-scale laboratory device the 50 % utilization was in fact reached.

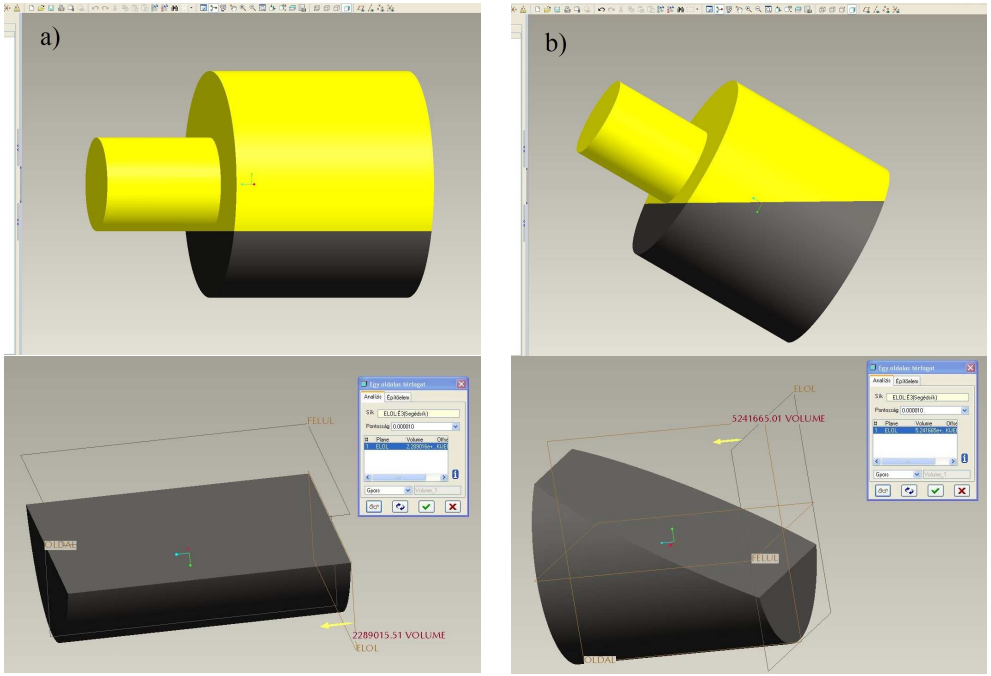

Figure 3. a) The effective volume of the horizontal layout reactor with the reactor neck b) The effective volume of the reactor with the reactor neck tilted by 30°

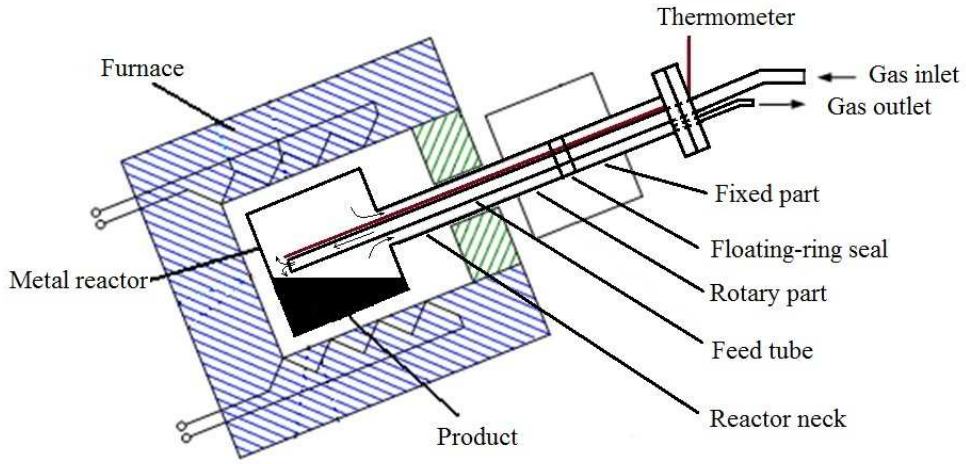

Figure 4. Scheme of the implemented large-scale laboratory device

The next task was to design a pilot device based on the large-scale laboratory device which had twenty times the effective volume of the latter.

The design was based on chemical similarity. The basis of similarity is that the product of the reaction rate and the average residence time must be the same. The average residence time is determined by the flow circumstances. The factors determining the reaction rate are the temperature and the initial concentrations. The two systems are chemically similar if the residence times are identical, provided that the temperatures and the initial concentrations are the same in the two systems. The identity of the initial concentrations can be solved readily. The temperature and the residence time however, need calculations.

During the design, we had to take the observations from the large-scale laboratory device into consideration. The product has heat-insulating properties. The required temperature for the reaction (750 ℃) is supplied by the furnace through the surface of the reactor. The thicker the layer of product, the bigger the heat-insulating effect is. This causes a decrease in the temperature inside the reactor. The problem could be solved with the pre-heating of the gases, but this is not practical because of the high temperature and the construction used. It is expedient to design the device so that it is longer and it has a smaller diameter, to have the smallest possible layer thickness of the product. The lower limit of the diameter of the pilot reactor is regulated by the maximum of the axial velocity (v_{ax}) of the gas. The high axial gas velocity can blow the product out of the reactor causing obturation in the flue pipe. The axial velocity of the gases cannot exceed $v_{ax,max}$=0.015 m/s in the reactor. It is important to note that the axial velocity and volume flow of the gases, and the residence time in the reactor is applicable for 750 ℃, the volume flow of the le aving gas however, was measured at 20 ℃.

The effective volume of the pilot reactor (abbreviated as pilot) should be twenty times bigger than that of the large-scale laboratory device ($V_{pilot,eff}=20V_{lsr,tilted,eff}$), thus $V_{pilot,eff}$=58 dm^3. Presuming a 50 % utilization, the total volume of the pilot reactor is V_{piolt}=116 dm^3. The volume flow leaving the large-scale reactor is 72 dm^3/h at 20 ℃, which is $7 \cdot 10^{-5}$ m^3/s at 750 ℃. This volume flow passes through the cross-section of a circle the diameter of which is 194 mm (A_{lsr}=0,0295 m^2). The axial velocity of the gas is $v_{ax,lsr}$=0.0024 m/s. The volume flow of the leaving gas in the pilot reactor is twenty times the volume flow of the large-scale laboratory device, which is $1.4 \cdot 10^{-3}$ m^3/s at 750 ℃. The diameter of the pilot reactor has to be as small as possible, but the axial gas velocity inside can only be at most $v_{ax,max}$=0.015 m/s. Thus the minimal diameter of the pilot reactor can be calculated as follows: $v_{ax,max} d_{pilot,min}^2 \pi/4 = 1.4 \cdot 10^{-3} m^3/s$ from which $d_{pilot,min}$=340 mm. The maximal reactor length for the minimal diameter is $l_{pilot,max} = V_{pilot}/(d_{pilot,min}^2 \pi/4)$=1280 mm.

The average residence time (τ) in the large-scale reactor is 74 s. The aim is that the average residence time be the same in the pilot reactor. The reactor is designed for the 70 % of the maximal axial gas velocity,

which is $v_{ax,pilot}=0.7v_{ax,max}=0.011$ m/s. The length of the reactor must be $l_{pilot}=\tau\ v_{ax,pilot}=810$ mm. From this the diameter of the reactor can be calculated, $d_{pilot}=420$ mm. For simple implementation, the length of the pilot reactor was chosen to be $l_{pilot,impl}=800$ mm and the diameter $d_{pilot,impl}=400$ mm. The volume of the implemented pilot reactor is $V_{pilot,impl}=100dm^3$. The construction is identical to the construction of the large-scale laboratory device. The diameter of the neck of the pilot reactor is 100 mm, the effective volume in horizontal alignment is 34 dm^3, illustrated in Fig. 5a. The inclination angle has to be determined at which the effective volume is approximately 50 % of the total volume. With the help of the Pro Engineer design software, we evaluated the effective volume of the reactor at different inclination angles. By tilting the reactor at 10°, the effective volume is 57 dm^3 (Fig. 5b).

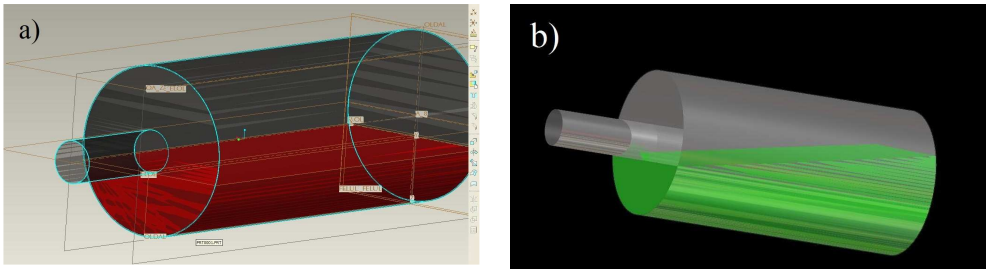

Figure 5. a) The effective volume of the horizontal layout pilot reactor
b) The effective volume of the pilot reactor tilted by 10°

To simulate the growing of nanotubes in our reactor, it is necessary to identify the rate of the growing process and the hydrodynamic behaviour of the reactor. The hydrodynamic behaviour of a system can be measured by simple physical experiments, e.g. by measuring the impulse or the step response of the system. In this study the step response of the reactor was measured. At first the reactor was filled with nitrogen in atmospheric pressure and at 750 ℃. The step function is genera ted by the hydrogen feed of the reactor. After the reactor was filled up with nitrogen, it is closed and the hydrogen was fed into the reactor with 72 dm^3/h. The hydrogen concentration was measured at the outlet point with a gas chromatograph. The collected data can be seen in Fig. 6. with black square markers.

The step response of the reactor is very similar to the step response of a perfectly mixed reactor (PMR), since the concentration of the hydrogen is much higher than zero even in the first sample, which is collected after 120 s. Hence, at the first step a concentrated parameter model has been developed to calculate the dynamic behaviour of the reactor. The gas phase is treated as ideal gas in the model. The average residence time, which can be calculated as the fraction of the total volume of the reactor

(5.63 dm^3), which involves the volume of the reactor neck and the reaction zone, and the volumetric flow rate of the reactor (72 dm^3/h), is 282 s. The solution of the PMR model of the reactor based on the total volume gives a small big difference from the measured values (see Fig. 6, dash line). In the developed PMR model the heat balance is not considered, however, there is a huge difference in the temperature of the neck and the reaction zone. As it can be seen in Fig. 6 the lack of the heat balance does not cause huge model error. However, the PMR model can be modified to achieve better fittings. It can be performed by decreasing the total reactor volume in the model (see Fig. 6, continuous line). The decreased volume is 5.35 dm^3. The fitted PMR model can be applied in our following work to understand the growing process of nanotubes. However, in the reactor sizing it cannot give any useful information.

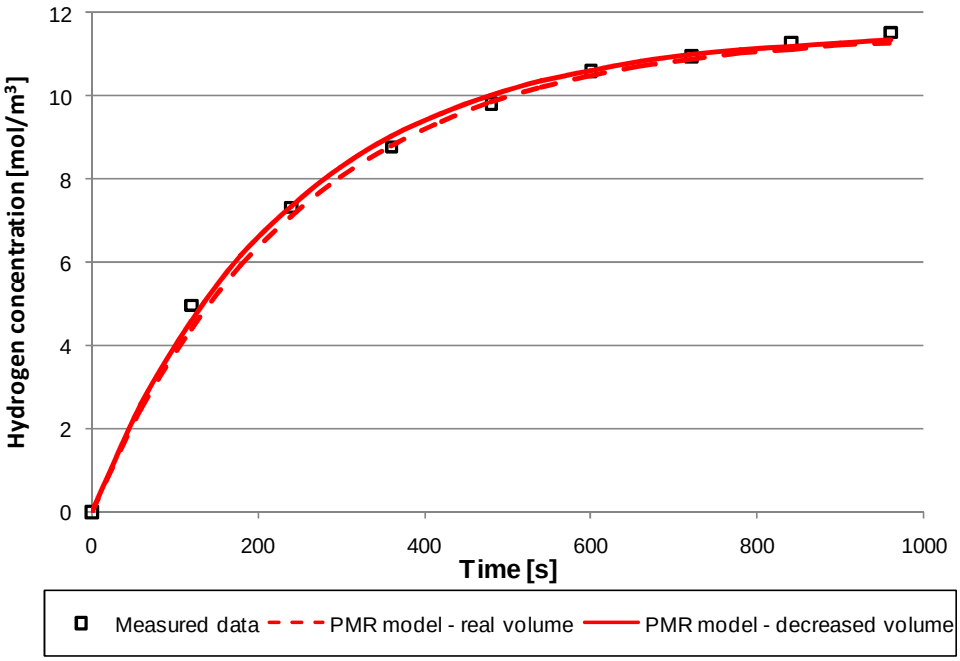

Figure 6. The measured and the calculated step response based on the PMR model of the reactor

Due to the high reactor temperature the diffusion coefficients of the gas molecules are very high which can be further increased by the developed turbulent flow in the reactor. To simulate the effect of the diffusion and to calculate the flow field in the reactor a distributed parameter model has to be worked out. Hence, a distributed parameter model has been developed in COMSOL Multiphysics to support the reactor

sizing process. COMSOL Multiphysics is more than just a software which uses CFD code, since mathematical models of different processes in many area of science are collected and classified; consequently the necessary time to solve an engineering problem is less than with applying other CFD software. COMSOL applies the finite element method to discretize the investigated object and to solve the implemented model [9].The first step of model building in COMSOL is the selection of the necessary correlations from the model collection. Of course there is a possibility to introduce new ones.

Since the reactor is axial symmetric, it can be investigated in two dimensions. The simplified geometry can be seen on the left side of Fig. 7. To calculate the flow field k-ε turbulence model is applied. The calculated steady-state flow field can be seen on the right hand side of Fig. 7. The red lines in this figure represents the streamlines, which show the path of the gas. The color of the surface represents the velocity in that point of reactor in m/s. The higher the velocity the lighter of the color in that point. The velocity is the highest in the feed tube and after the gas escapes to the reaction zone gets much slower due to the increase in the volume.

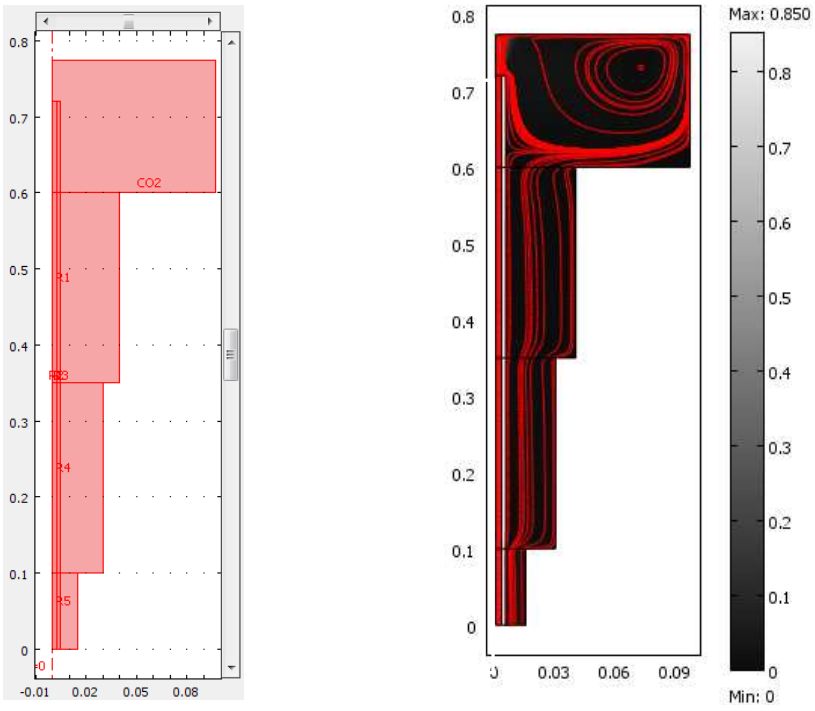

Figure 7. The investigated geometry and the calculated flow field in the laboratory reactor

A component balance has been added to the CFD model to calculate the concentration of hydrogen in the reactor. The step response of the developed CFD model can be seen in Fig. 8 comparing with the measured data. The diffusion coefficient of the hydrogen is the only unknown parameter of the developed model, although there are many correlations in the literature which can be used to calculate this value at high temperature. In this study, the value of diffusion coefficient is identified but in the further work the correlations found in literature for the calculation of diffusion coefficient is tested and added in the model.

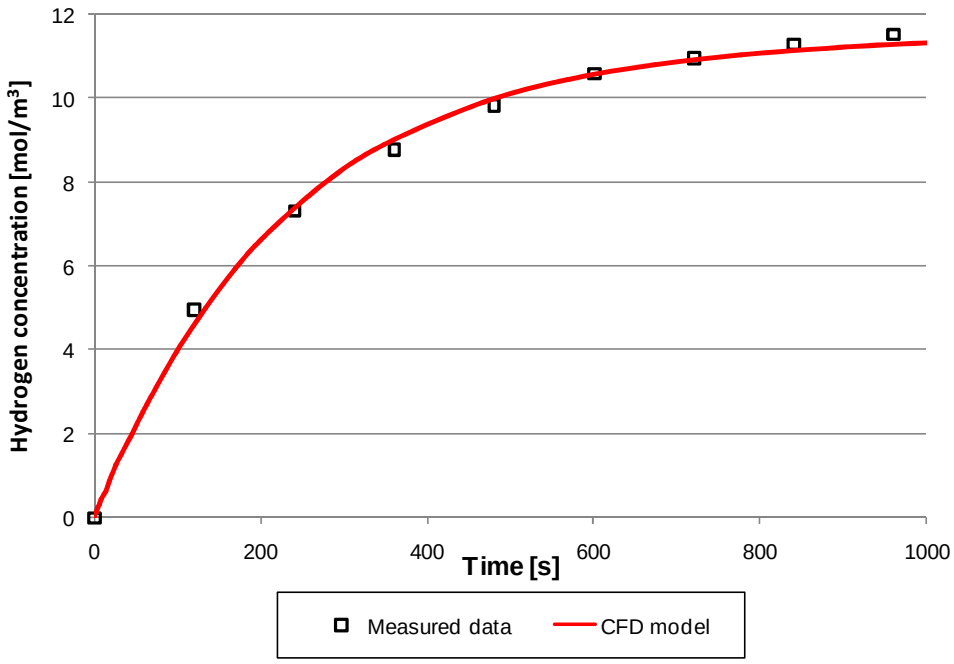

Figure 8. The measured and the calculated step response based on the CFD model of the reactor

Based on the CFD model, the average velocity in the reaction zone is 1.49e-2 m/s when there is not solid phase in the reactor. The average velocity is calculated as a volume integral in the reaction zone. Our purpose is to achieve the same average velocity in the reaction zone of the new reactor in which the length of the feed tube can be modified. Hence, the effect of the length of the feed tube on the developed flow field and the average velocity is investigated based on the CFD model of the new reactor.

The calculated flow fields in the new reactor in case of different feed tube length can be seen in Fig. 9. As the feed tube is pushed deeper and deeper into the reaction zone, the swirling part of the zone is getting smaller and smaller. Hence, the mixing in the reaction zone is from bad to worse. The average velocity in the three cases is plotted in Fig. 10 where the horizontal dashed line represents the desired velocity, which belongs to the large-scale laboratory reactor. This simulation experiments show, that similar flow field can be achieved in the new reactor, if the length of the feed tube is about 0.5 m in the reaction zone.

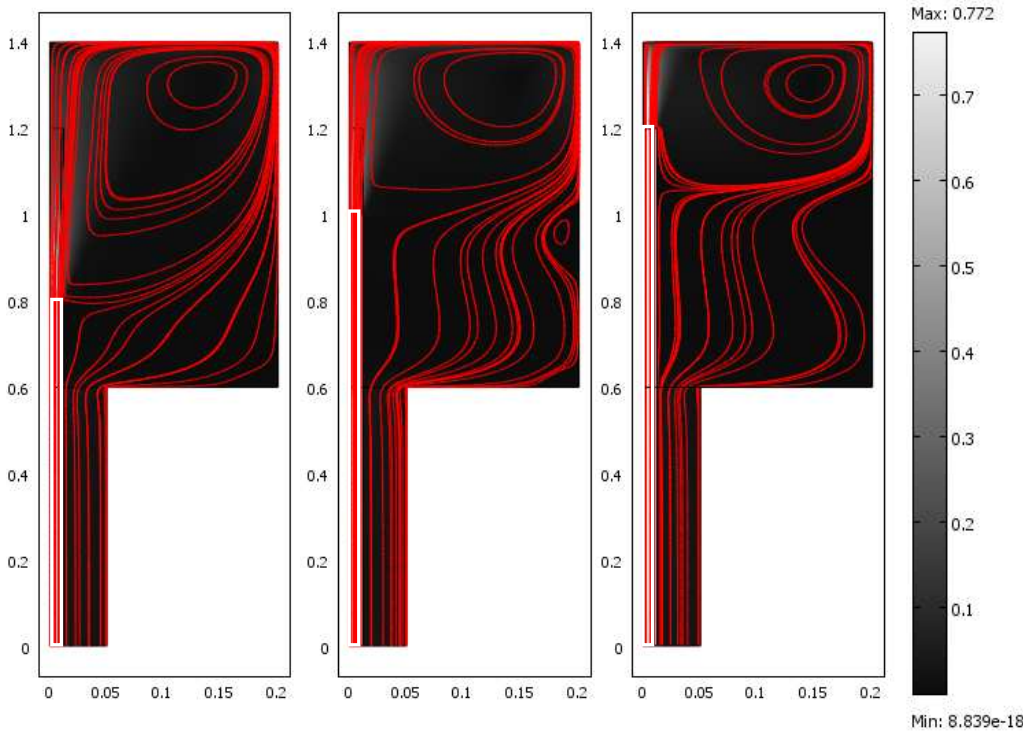

Figure 9. The developed flow field in case of different inlet tube length

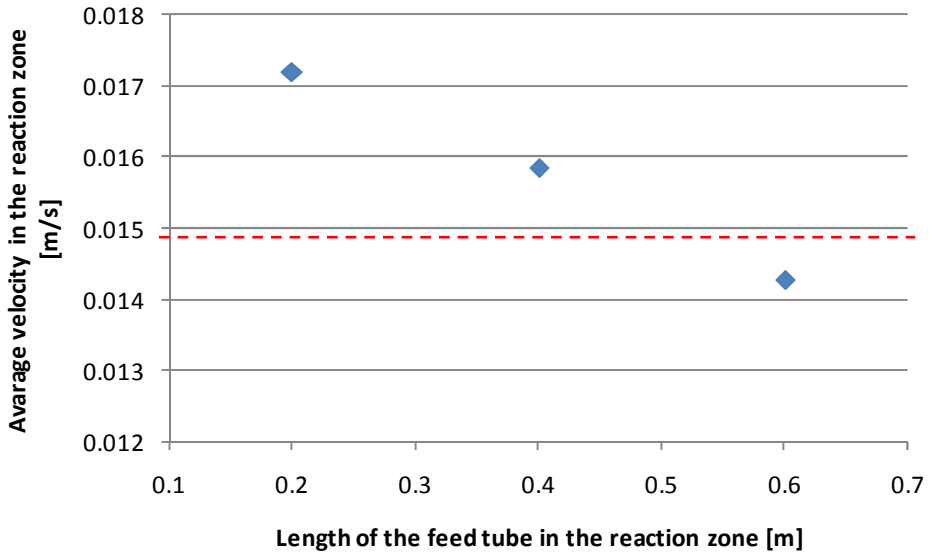

Figure 10. The effect of inlet tube length on the average velocity in the reaction zone

CONCLUSIONS

A large-scale laboratory device was planned and implemented on the basis of a smaller laboratory device. A pilot device was planned based on the observations and the experiments conducted with the large-scale laboratory device. The size of the large-scale laboratory reactor was calculated by the mechanical similarity. After the implementation of the large-scale reactor physical experiments were performed to collect information about the behaviour of the reactor. Based on these experiences a pilot reactor was planned using chemical similarity. CFD simulations were performed to understand the developed flow field in the reaction zone. Based on these simulations the length of the feed tube of the pilot reactor was determined.

ACKNOWLEDGMENTS

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